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Historical perspective

An overview of the transport of liquid molecules through structured polymer films, barriers and composites – Experiments correlated to structure-based simulations

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ABSTRACT

Films engineered to control the transport of liquids are widely used through society. Examples include barriers in packaging, wound care products, and controlled release coatings in pharmaceutics. When observed at the macroscopic scale such films commonly appear homogeneous, however, a closer look reveals a complex nano- and microstructure that together with the chemical properties of the different domains control the transport properties. In this review we compare and discuss macroscopic transport properties, measured using the straightforward, yet highly powerful technique "modified Ussing chambers", also denoted side-by-side diffusion cells, for a wide range of structured polymer films and composites. We also discuss and compare the macroscopic observations and conclusions on materials properties with that of lattice Boltzmann simulations of transport properties based on underlying material structure and chemistry. The survey of the field: (i) highlights the use and power of modified Ussing Chambers for determining liquid transport properties of polymer films, (ii) demonstrates the predictability in both directions between macroscopic observations of transport using modified Ussing chambers and structure-based simulations, and (iii) provides experimental and theoretical insights regarding the transport-determining properties of structured polymer films and composites.

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1. Introduction

People use different types of barriers in their daily life, for examples in packaging, wound care products, and pharmaceutical coatings [1–4]. Many barriers today are based on polymers due to reduced costs, fast production etc. [5]. Polymeric barriers can be produced via a wide range of methods including extrusion, spray coating, casting, moulding etc., where the choice of technique depends on the final application. Different approaches will also result in different types of material structures: the reader is refereed to Fig. 1 for an overview of examples of structures discussed in this review. Combinations of different polymers are often essential to obtain all desired characteristics of the final application.

Non-porous/dense films and laminates are examples of common structures in different types of packaging. In these cases the properties of the polymers are combined, and one layer may serve as an oxygen barrier, while another layer may function as a moisture barrier, whereas the third layer provides the consumer with information about the content [2,6]. A composite is a material that consists of a polymer matrix and a filler. These materials can also be used as packaging materials [7]. Here, the filler is commonly included to enhance the mechanical properties of the material and the particles are generally considered to be impermeable. Thus, an addition of filler should in theory result in improved barrier properties [8,9]. However, in reality, incompatibility between the filler and the matrix due to the differences in the surface chemistry may result in voids in the material and an increased permeability as a consequence [10–12].

Materials with controlled transport properties can also be formed by combining polymers with limited miscibility. For example, by a suitable combination of water-soluble and water-insoluble polymers, a film can be formed where the components have phase-separated into distinct regions [13]. Upon exposure to water the soluble component will leak out, leaving a porous skeleton of the water-insoluble polymer [14–17]. Porous films are commonly used as pharmaceutical coatings, and the pores can be either connected or disconnected depending on the desired release profile, where the connected pores are expected to result in a faster release of a pharmaceutical active ingredient. By varying the composition and/or the preparation conditions, the transport properties of such films can be controlled with great precision [15,18,19]. A complicating factor in predicting the transport through coatings/films in complex environments is that polymers are prone to swell in compatible solvents and that the diffusion in polymer matrixes is strongly dependent on the volume fraction of polymer [20]. An increase in the diffusion coefficient with decreasing volume fraction of polymer may also be counteracted by the swelling, causing blockage of pores, and an increased diffusion distance due to macroscopic volume increase. For example, this has been shown to be of relevance to the performance of pharmaceutical controlled release coatings in presence of alcohol [21] since there is a risk of dose dumping [22]. The latter might result in a peak in the plasma of the drug, which can have fatal consequences for the patient.

Factors known to affect the rate of transport through a membrane are, for example, crystallinity, type and concentration of fillers, compatibilizers and/or plasticizers, as well as the chemical structure of the polymer (molecular weight, degree of cross-linking, taciticity etc.). In general, two types of models are used to explain the permeability and the mass transport mechanisms in polymer materials: (i) models based on the motion of polymer chains and the permeant in combination with intermolecular forces, and (ii) models with a foundation in free volume theory, considering the relationship between the diffusion coefficient and the free volume present in the polymer [23]. Extensive reviews of these models can be found elsewhere [20,24].

The most important property for barrier materials is however to withstand the transport of liquids and gases in both and/or one direction, for example to protect a product from the environment, and thereby avoid degradation/contamination. Even though the films may seem homogenous from a macroscopic point of view, it may differ significantly on the micro- and nanoscopic level. To be able to design materials with desired properties it is crucial to understand the structure-transport correlations, which can be performed either by measuring or simulating the permeability. For this purpose, it is of importance to study both the gas permeability and the transport of solvent molecules or molecules dissolved in solvent (liquid permeability). Several reviews on gas transport are available in the literature [25–28]. Liquid permeability can be advantageously measured by utilizing modified Ussing chambers, which is an experimental setup for measuring the diffusion of permeants through a barrier material. The original chambers were invented by a Danish zoologist and physiologist named Hans Henriksen Ussing and the main idea is to measure the vectorial ion transport through epithelial skin [29]. The chambers have also been used to measure the transport of ions, nutrients, and drugs across epithelial tissues in vitro [30,31]. Side-by-side diffusion cells are also commonly used and resemble modified Ussing chambers. The latter can be used for many different purposes related to diffusion, and the focus of this review will be on studies where molecules, such as water, different pharmaceutical drugs, and juice ingredients, have been used to measure transport over different types of barriers.

The aim of this review is to present the applicability of using modified Ussing chambers and side-by-side diffusion cells to correlate diffusion through complex materials to their structures on nano- and

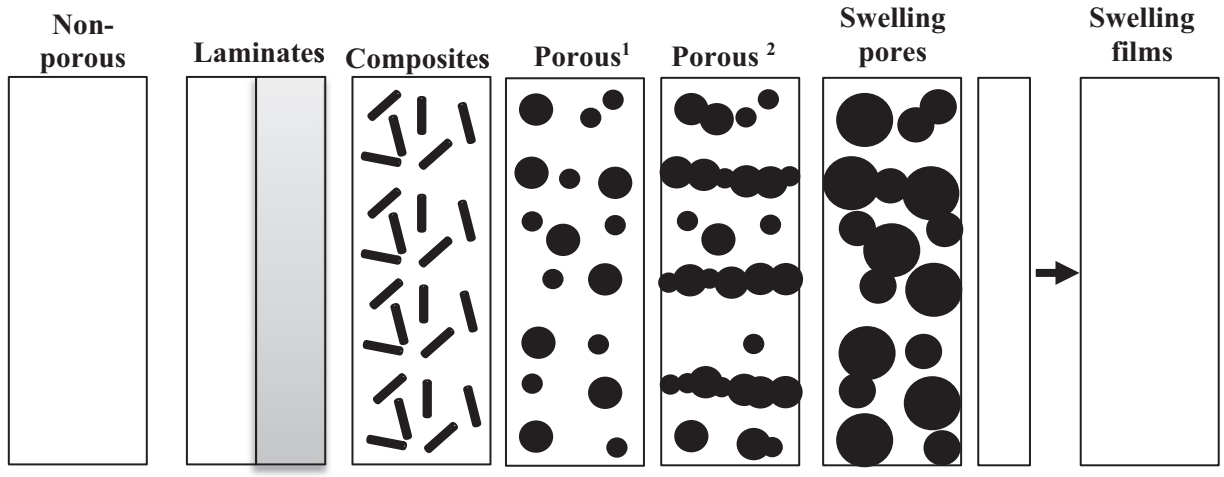

Fig. 1. Schematic drawings of different film structures discussed in this review, (1) corresponds to disconnected and (2) to connected pores.

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